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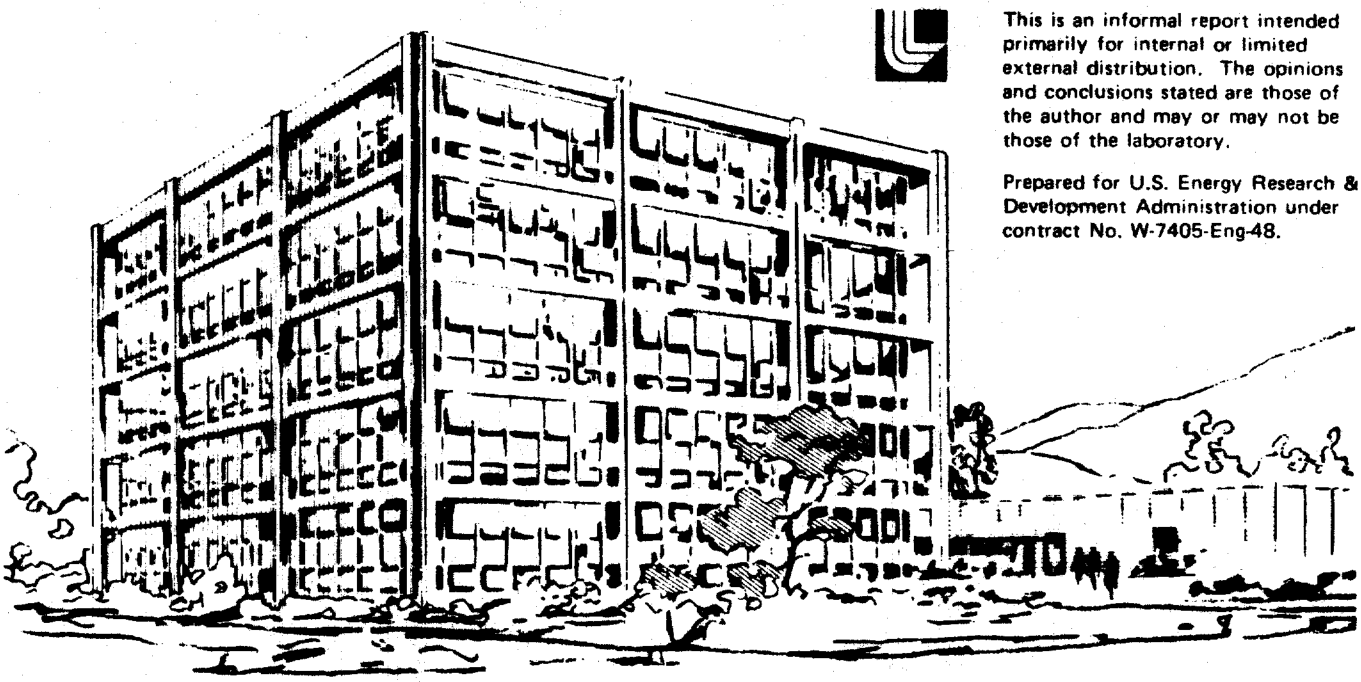

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R. K. Pearson

Abstract

The gas phase thermal reaction of UF_6 with SiH_4 begins at ~135°C producing fluorosilanes, predominantly SiH_3F, as volatile products along with some non-volatile black solids. Both unreacted SiH_4 and UF_6 were present with SiH_3F after 25 min at 145°C.

Introduction

This reaction was carried out to obtain rough estimates of the gas phase activation energy of the reaction between SiH_4 and UF_6 for comparison with matrix isolation experiments using single photon excitation.[(1)] If we adopt the viewpoint that, for a gas phase bimolecular thermal reaction between SiH_4 and UF_6, there exists a collisional transition state complex intermediate whose decomposition is unimolecular, we can estimate an apparent activation energy using first order kinetics from the instantaneous reaction rate.[(2)] We obtain an approximation of the apparent activation energy for a "normal" first order decomposition by simply determining the threshold temperature at which reaction begins. Our approach was to mix the gases in a heated Monel vessel for a given period of time at the indicated temperature and then quench the gases to room temperature and obtain infrared spectra of the gaseous reaction mixture.

Experimental

The apparatus used was a Monel vacuum line which had been conditioned successively with gaseous ClF_3 and UF_6 by allowing each gas to remain at several hundred torr overnight. A Monel reactor of about 100 ml volume was surrounded by a furnace whose temperature was controlled by means of a thermoregulator.

The UF_6 was expanded into the reactor and its pressure read on a capacitance manometer. The valve to the reactor was closed and the UF_6 removed from the manifold by pumping. Silane was then allowed to flow into the manifold to the calculated pressure greater than that of the UF_6 in the reactor. The valve to the reactor was then opened for several seconds to allow the SiH_4 to flow into the reactor along with the UF_6. A reading of the pressure transducer gave the total pressure in the reactor. A timer was activated on mixing and was read at the time the mixture was quenched and allowed to flow into an 8 cm Monel-body, infra red cell with AgCl windows at room temperature. A scan was then made to observe whether any new bands other than starting materials were present.

Results and Discussion

A summary of the experiments carried out to obtain the threshold temperature at which UF_6 and SiF_4 begin to react is presented in Table I. Since no reaction was detectable at 100^oC in 20 min and reaction was complete at 157^oC in 240 min, the threshold temperature lies between these values. At 145^oC in 25 min the reaction mixture still contained both UF_6 and SiH_4. Thus the threshold of reaction lies between about 130^oC and 140^oC. If we take 135^oC as the temperature at which we might reasonably expect to get about 10% reaction in 5 min we obtain an estimated first order

Table I. Summary of Experiments of the Gas Phase Reaction of SiH_4 with UF_6.

Exp.	UF_6(a) Pressure (Torr) in Reactor	SiH_4(a) Pressure (Torr) in Reactor	Time (min)	Temperature ^{o}C	Total Pressure (Torr) in I.R. Cell	Results
1	40.2	48.2	30	25^{o}	51.0	No reaction. SiH_4 and UF_6 only
2	40.2	48.2	20	82^{o}	43.4	No reaction. SiH_4 and UF_6 only
3	40.4	48.2	240	157^{o}	28.2	All SiH_4 and UF_6 reacted. SiF_4 and fluorosilanes present.
4	40.7	33.8	20	100^{o}	30.2	No reaction. SiH_4 and UF_6 only
5	40.7	33.8	25	145^{o}	11.8	SiH_3F, strong bands; SiH_4, weak bands; UF_6 + ? present moderate bands

(a)Reference scans were made at several pressures of UF_6 and SiH_4 for comparison purposes prior to the experiments.

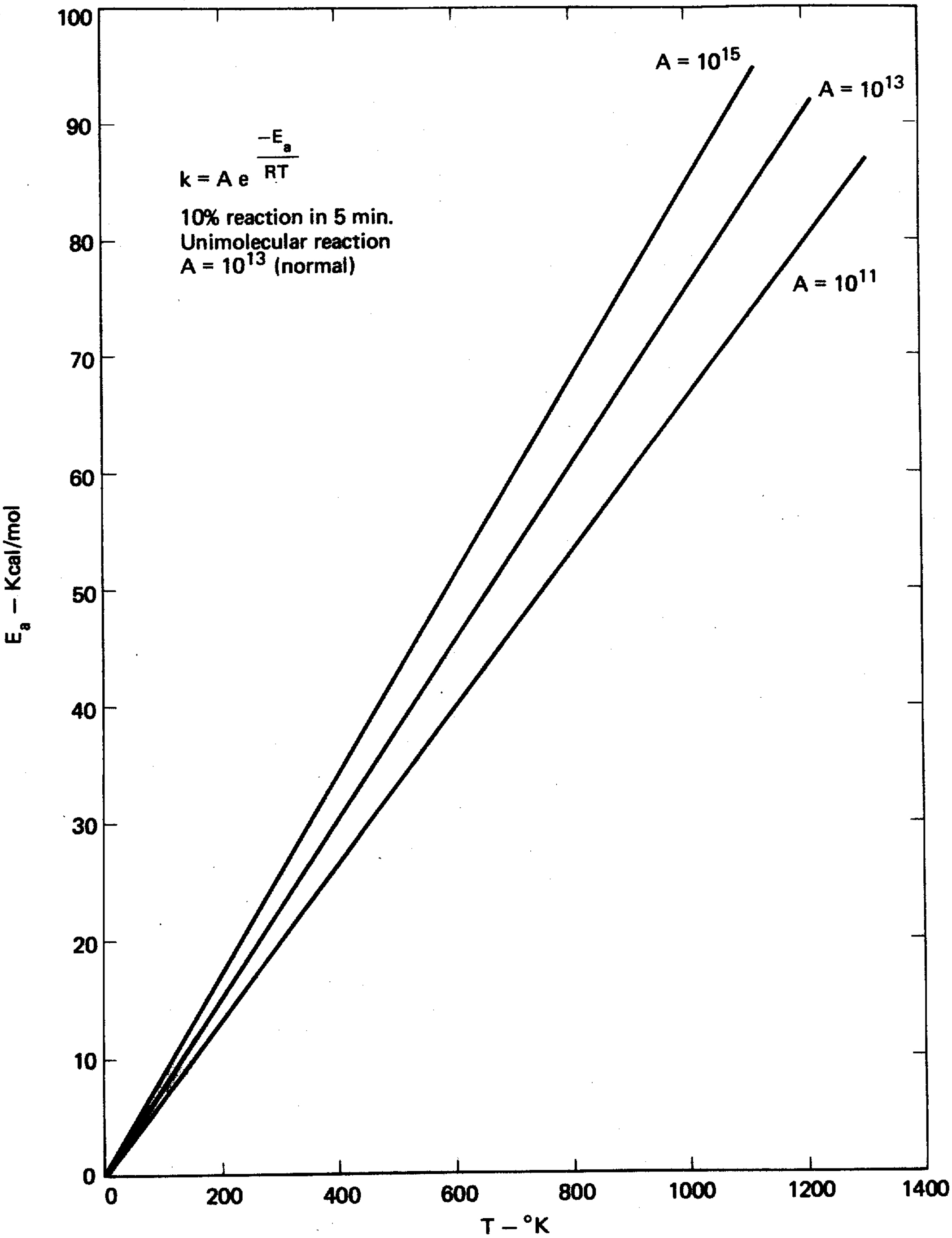
Ea of 31.6 kcal/mol (See Fig. 1) if the A factor is a "normal" value of 10^{13}. The A-factor for most first order gaseous decompositions lie between 10^{11} and 10^{15}, so a reasonable activation energy might be 31.6 $\pm$ 3.7 kcal/mol. The difference between 10% reaction and 90% reaction in 5 min corresponds to a difference in activation energy (constant A-factor) of 1.8 kcal/mol.

If we choose to apply this treatment to a bimolecular process, a pre-exponential factor or A-factor for a "normal" reaction is about 10^8 to 10^9 $l\ mol^{-1}\ sec^{-1}$.[3] Figure 2 shows bimolecular plots of Ea vs temperature for A-factors of 10^6, 10^8, 10^{10}, and 10^{12} for 10% reaction in 5 min with initial pressure of 40 torr which is comparable to our conditions. Using this plot an Ea = 16 kcal/mol is estimated.

The author is aware of the hazards of these kinds of approximations without knowledge of the reaction mechanism but until many further experiments are performed the value of an apparent Ea = 32 kcal/mol based on unimolecular kinetics or an apparent Ea = 16 kcal/mol based on bimolecular treatment is the best that can be estimated from the minimum temperature at which reaction is detectable.

Still another way of approximating a minimum value for Ea, assuming first order treatment, is to calculate a rate constant from the estimated "threshold temperature" of 135°C for 10% reaction in 5 minutes. When this rate value is combined with a maximum value for a rate at 100°C where the minimum detectable reaction was ~1% in 20 minutes (the extent of reaction detectable by our infra-red spectrum), a minimum value of Ea of 32 kcal/mole can be estimated.

Fig. 1. Plots of Ea versus temperature for unimolecular reactions of different A-factors for 10% reaction in 5 min.



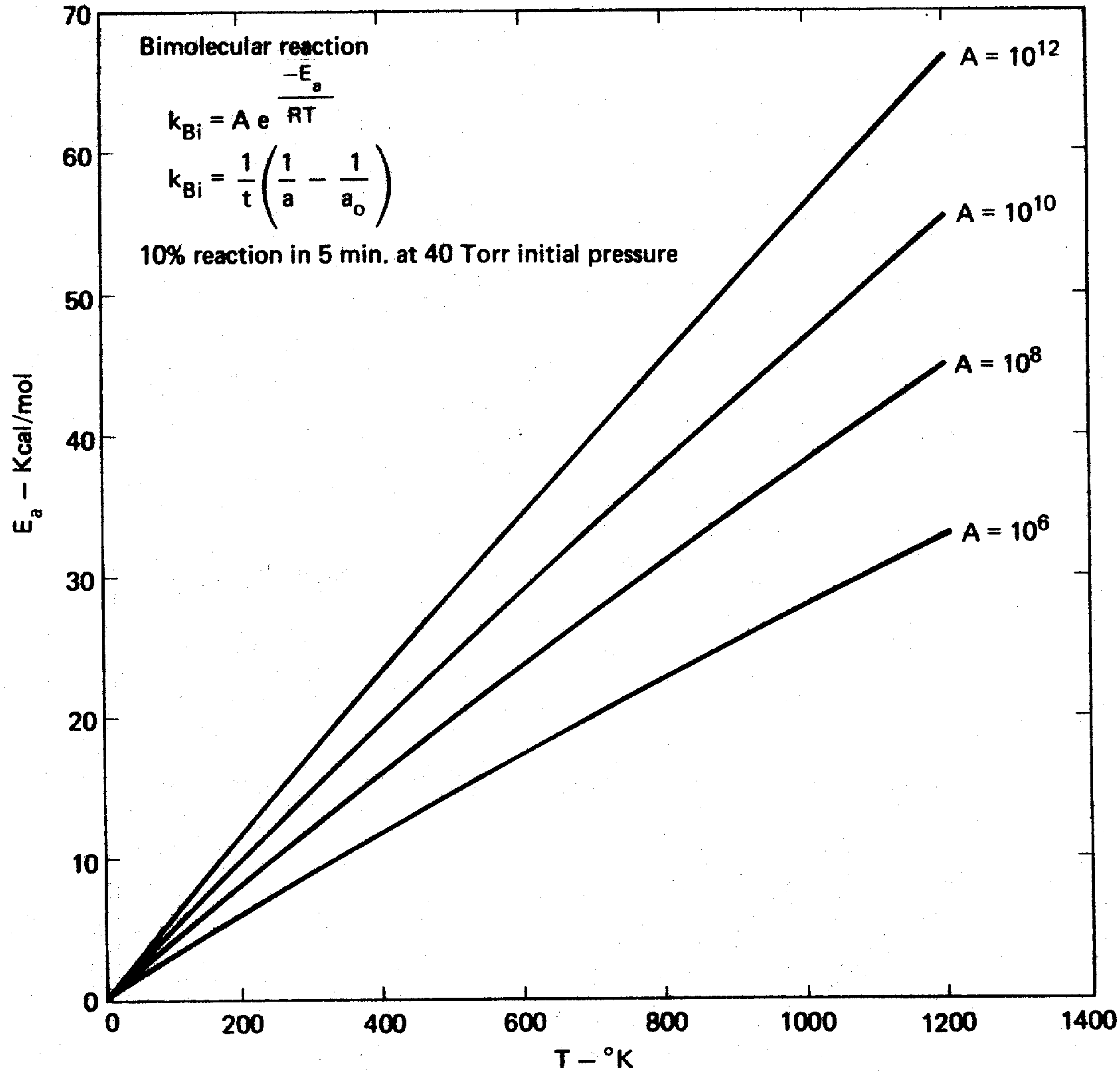


Fig. 2. Plots of Ea versus temperature for bimolecular reactions of different A-factor for 10% reaction in t min with an initial concentration of 40 Torr.

Bibliography

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